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13. ABSTRACT (Maximum 200 words)

The specific aim of this research program is to understand the cooperative magnetic properties of geometrically frustrated magnets which are model systems for the general phenomena of frustration. In the past year we have continued studies of the dynamic properties of a new type of frustrated magnetic system, the "spin ice" compound $Dy_2Ti_2O_7$. The spin ice materials are a class of frustrated magnets in which *ferromagnetic* interactions can be frustrated. The geometry of the lattice and the nature of the local spins in these materials result in low temperature thermodynamics which are remarkably analogous to frozen water. Our findings demonstrate that spin ice systems represent a new modality of spin freezing in a glassy system. We have found a variety of novel behavior in these materials, in particular a crossover from thermal to quantum spin relaxation which is reversed as spin-spin correlations develop, and a reentrant behavior of the spin freezing with dilution of the magnetic sublattice. We have also initiated studies of other frustrated magnetic materials as well as frustrated arrays of ferromagnetic nanostructures.

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(1) Problem Studied and Important Results

Geometrically frustrated magnetic materials, in which the topology of the spin lattice leads to frustration of the spin-spin interactions, have recently be demonstrated to comprise a new class of magnets in which a number of unique cooperative spin states have been observed. These systems are of particular importance because they offer a unique venue through which one can examine the consequences of frustration in the thermodynamic limit in a clean system (i.e. where disorder is not dominant). Understanding such frustrated systems has implications for systems as diverse as neural networks and Josephson junction arrays.

Although geometrical magnetic frustration has been most extensively studied in materials with antiferromagnetic nearest-neighbor interactions, the effects of strong frustration have also been found in the so-called "spin ice" materials in which *ferromagnetic* as well as dipolar interactions can be frustrated. In these compounds (such as $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Sn_2O_7$), the rare earth spins with a strong single-ion anisotropy localized on a tetrahedra-based pyrochlore lattice are governed by the same statistical mechanics as the hydrogen atoms in water ice. In the ground state of ordinary hexagonal ice (*Ih*), oxygen ions reside at the center of tetrahedra with two of the four nearest hydrogen ions (protons) situated closer to it that the remaining two. In spin ice materials, the magnetic rare-earth ions are situated on a lattice of corner-sharing tetrahedra and their spins are constrained by crystal field interactions to point either directly toward or directly away from the centers of the tetrahedra. Dipole and ferromagnetic exchange interactions between the spins require that, on each tetrahedron, two spins point inward and two point outward in exact analogy to the protons in ice. In both systems, there is a large degeneracy of states which satisfy the energetic requirements and therefore novel low temperature behavior associated with this frustration.

The spin ice state has been demonstrated experimentally through neutron scattering studies and also through measurements of the magnetic specific heat, which yield a measured ground state entropy in exact agreement with the theoretical prediction for the "ice rules" (first codified by Pauling) and experimental results for ice. While the spin entropy only freezes out below $T \sim 3$ K in $Dy_2Ti_2O_7$, our recent magnetic susceptibility studies show a strongly frequency dependent cooperative spin-freezing at $T \sim 16$ K. In contrast to traditional spin glasses (in which disorder leads to frustration of local spin-spin interaction), the spin-freezing transition was shown to be associated with a very narrow range of relaxation times, presumably attributable with the onset of local ice-like correlations among the spins. Furthermore, rather than quenching the spin-freezing as in spin glasses, application of a magnetic field is found to enhance the spin ice freezing. The dynamic spin-ice freezing in $Dy_2Ti_2O_7$ is therefore a rather unusual example of glassiness in a magnetic system. We have studied spin relaxation in this system as a function of temperature and magnetic field. We find an unusual crossover from thermal to quantum spin relaxation with decreasing temperature. This crossover is, however, reversed as strong spin-spin correlations develop at the lowest temperatures during the freezing into the spin ice ground state. We have studied the spin freezing which develops at lower temperatures ($T < 4$ K) as a result of this re-entrance and shown it to be quite different from the spin freezing in ordinary spin glasses in that there is again a very narrow range of spin relaxation times. We also have studied this system as a function of dilution with non-magnetic ions, and we find unusual behavior in that dilution first decreases and then increases the spin relaxation time, resulting in the suppression and subsequent enhancement of the spin freezing with dilution – something which is possibly unique in glassy magnetic systems.

Due to the purity of the system, spin ice provides an excellent venue in which to study a simplified model of the complex thermodynamics of ice as well as the more general consequences of frustration in the limit of low disorder. Furthermore, because the frustration is associated with uniaxial spins (rather than Heisenberg spins), these systems are more analogous to the artificial frustrated spin systems which we are currently studying under another grant, after initiating studies under this grant.

While most of the research under this grant has been of the spin ice system, the funds have also supported the initiation of the studies of artificial frustrated systems (created through lithography) as well as studies of other frustrated magnetic materials which are now being continued with NSF support.

(2) Publications (all are in peer-reviewed journals)

"Re-entrant Behavior of a 3D Spin Liquid Phase and Analog to the ^{4}He Melting Curve in a Geometrically Frustrated Magnet," Y.K. Tsui, J. Snyder, and *P. Schiffer* Canadian Journal of Physics **79**, 1439–1446 (2001).

"Thermodynamic Study of Excitations in a 3D Spin Liquid," Y.K. Tsui, J. Snyder, and *P. Schiffer*, Physical Review B **64**, 012412-1 - 012412-4 (2001).

"How spin ice freezes," J. Snyder, J. S. Slusky, R. J. Cava, and *P. Schiffer*, Nature **413**, 48 - 51 (2001).

"Dirty Spin Ice: The Effect of Dilution on Spin Freezing in $Dy_2Ti_2O_7$" J. Snyder, J. S. Slusky, R. J. Cava, and *P. Schiffer* Physical Review B **66**, 064432 - 1 – 064432 –5 (2002).

"Quantum-Classical Reentrant Relaxation Crossover in $Dy_2Ti_2O_7$ Spin-Ice" J. Snyder, B. G. Ueland, J. S. Slusky, H. Karunadasa, R. J. Cava, Ari Mizel, and P. Schiffer Physical Review Letters 91, 107201-1-4 (2003).

"Ba_2LnSbO_6 and Sr_2LnSbO_6 (Ln = Dy, Ho, Gd) double perovskites: Lanthanides in the geometrically frustrating fcc lattice" H. Karunadasa, Q. Huang, B. G. Ueland, P. Schiffer, and R. J. Cava, Proceedings of the National Academy of Science **100**, 8097-8102 (2003).

"Low Temperature Spin Freezing in $Dy_2Ti_2O_7$ Spin Ice", J. Snyder, B. G. Ueland, J. S. Slusky, H. Karunadasa, R. J. Cava, and P. Schiffer, Physical Review B **69**, 064414-1-6 (2004).

"Quantum and thermal spin relaxation in diluted spin ice: $Dy_{2-x}M_xTi_2O_7$ (M = Lu, Y)" J. Snyder, B. G. Ueland, Ari Mizel, J. S. Slusky, H. Karunadasa, R. J. Cava, and *P. Schiffer*, Physical Review B (in press, 2004).

(3) Scientific Personnel Supported

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Benjamin Ueland (Ph.D. Student)
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Joseph Snyder (Ph.D. student who received his degree in 2003)

(4) Report of Inventions

none